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**by**

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**Surface Reconstruction and Templating for Zeolite Thin Film Synthesis  
Observed by Atomic Force Microscopy**

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Atomic force microscopy (AFM)<sup>1</sup> allows one to nondestructively image insulating surfaces in air or under liquids with molecular resolution<sup>2-6</sup>. When applied to zeolites<sup>7</sup> this technique allows observation of real time processes of crystal structure<sup>8</sup> on the external surface of a single crystal under water, salt solutions or alcohols<sup>9</sup>. It also offers the opportunity to directly observe surface reconstruction using solution cationic templates to generate new zeolitic thin film phases. In this study, AFM was used to monitor room temperature lattice reconstruction on the surface of a natural single crystal of stilbite using sodium ion templates to form a new periodic lattice. This is the first reported application of AFM for the investigation of reconstructive chemistry of a nonconducting surface.

The natural zeolite crystal stilbite<sup>10</sup> was imaged with an AFM before and after soaking it in a concentrated 5M NaOH. Figures 1a,b show the crystal surface at low magnification. Figure 1a reveals the typical step-structure of a stilbite (010) surface, as it is expected for a single crystal. A polycrystalline structure of the same crystal after soaking it in 5M NaOH aqueous solution at room temperature can be seen in Figure 1b. There are no more steps and preferred direction recognizable, but only cluster structure which might move such crystal domains.

The molecular structure of these crystals can be resolved by increasing the magnification. Figure 2a shows an image of stilbite (010) before it was soaked in 5M NaOH, while Figures 2b and 2c were taken after the same crystal<sup>8</sup> was soaked for 30 minutes in 5M NaOH outside the AFM at room temperature. Note that Figure 1b was collected after this crystal was soaked for another 12 hrs. at room temperature in 5M NaOH. The measured repeating distances of the untreated stilbite (010) surface are  $6.5 \pm 0.6 \text{ \AA}$  in the  $51 \pm 5^\circ$  direction (measured counterclockwise from the positive x-axis) and  $5.3 \pm 0.5 \text{ \AA}$  in the  $173 \pm 2^\circ$  direction which agrees well with the known spacings and angles ( $1/2a = 6.8 \text{ \AA}$ ,  $1/2c = 5.6 \text{ \AA}$ ,  $\angle = 128^\circ$ )<sup>9</sup> (see Figure 4a). The repeating distances for the soaked crystal surface are  $4.8 \pm 0.5 \text{ \AA}$  in the  $37 \pm 2^\circ$  direction,  $4.5 \pm 0.5 \text{ \AA}$  in the  $107 \pm 2^\circ$  direction. (Note to reduce the effect of drift while imaging, an up and a down scanning image were averaged). These repeating distances cannot be matched within the end bars with the known data for stilbite (010), and a surface reconstruction must have occurred

while soaking it in 5M NaOH.

The discovery of the surface reconstruction with an AFM led to more structural investigation using powder X-ray diffraction. One might expect that the crystal would merely dissolve in concentrated NaOH solution, or that an amorphous aluminosilicate coating would cover the crystal. This not being the case, what phases might one expect from this reaction? To answer that question, a powder sample of stilbite was prepared by grinding natural stilbite crystals, and powder X-ray diffraction was performed. This sample was then reacted with 5M NaOH at 100°C for 12 hours. A powder pattern was again obtained, and Figure 3 compares the results. Notice that the characteristic lines for stilbite have disappeared. The new lines are consistent with the sodalite structure (Fd3m;  $a = 8.8761(1) \text{ \AA}$ ), with the exception of weak lines at 7.4, 16.2, 29.0, 29.9, and 49.3° two theta ( $l = 1.51/19 \text{ \AA}$ ) which are suggestive of zeolite A spacings ( $a = 24.6 \text{ \AA}$ ).

The fact that another zeolitic phase is formed from this reaction is quite surprising. The hydrothermal, synthetic conditions for the formation of crystalline zeolitic phases depend on complicated kinetic schemes and phase equilibria which have been described by Barrer, among others. The conditions described above are extremely far from ideal synthetic conditions for the formation of sodalite, which is normally synthesized from an amorphous gel derived by mixing colloidal silica and a sodium aluminate solution in the appropriate molar ratios, followed by heating. The Si:Al ratio in stilbite of 3:1 is rather high for sodalite which normally forms with a framework Si:Al ratio near unity. Having a small amount of Ca in the stilbite should not be too much of a problem given the enormous concentration of Na ions in the surrounding solution. Sodalite is, however, the thermodynamic sink in the zeolite X, A, sodalite series, and might be formed if some kind of equilibrium condition were reached.

Since we can exclude the possibility that treated crystal is stilbite (010) at the surface - also suggested by X-Ray powder data - we have to consider all of the other possibilities for an interpretation: sodalite surface, zeolite (111) surface, and close packed 6-rings.

Laue photographs and "powder" diffraction performed on the (010) face of the single crystal used in the AFM experiments were inconclusive as to the nature of the surface phase. This is most likely due to the fact that the vast majority of the crystal was unreacted stilbite (in reality, probably only a few monolayers of reconstructed surface were

formed on the crystal given the short contact time with the solution at room temperature). The lattice observed by AFM is not that of sodalite, but has some resemblance to the spacings indicated for the (111) face of zeolite A (Figure 4). Additional studies using low angle synchrotron scattering are planned in order to properly identify the surface phase.

These findings suggest a new approach to the formation of zeolite thin films. AFM can be used to monitor the surface structure and chemistry which leads to the formation of microporous thin films, and further to characterize not only the materials formed, but the interaction of molecules at the surfaces. The self assembly of organic cationic groups on single crystal surfaces, the covalent fastening of organic substituted cationic ligands by silylation reactions on mica, and the use of Cd arachidate to anchor organic groups on mica has been previously demonstrated by AFM. These approaches along with the use of inorganic cations which coordinate to the anionic substrate surface provide alternative mechanisms for the templating necessary for thin film synthesis.

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**Figure Captions:**

- Figure 1a. Large scale image of stilbite (010) surface in 0.1 M NaOH aqueous solution. The image size is  $3200 \text{ \AA} \times 3200 \text{ \AA}$ , the height is about  $70 \text{ \AA}$ .
- Figure 1b. Large scale image of "stilbite (010)" surface in 0.1 M NaOH aqueous solution after soaking it in 5M NaOH over night. The image size is  $3000 \text{ \AA} \times 3000 \text{ \AA}$ , the height scale is about  $35 \text{ \AA}$ .
- Figure 2a. Molecular scale image of stilbite (010) surface imaged in 0.1 M NaOH aqueous. The image size is  $100 \text{ \AA} \times 100 \text{ \AA}$ .
- Figure 2b. Molecular scale image of "stilbite (010)" surface imaged in 0.1 M NaOH aqueous, after it was soaked in 5M NaOH for 30 minutes and before it was soaked over night for Figure 1b. Image size  $100 \text{ \AA} \times 100 \text{ \AA}$ .
- Figure 2c. Even higher magnification of same surface as in Figure 2b. Image size  $50 \text{ \AA} \times 50 \text{ \AA}$ .
- Figure 3. Powder X-Ray diffraction pattern of stilbite that was not treated and of stilbite, that was soaked in 5M NaOH for 12 hrs at  $100^\circ \text{ C}$ .
- Figure 4. Computer simulated structure of zeolite A (111) surface ( $a = b = c = 24.61 \text{ \AA}$ ). For the stilbite (010) surface  $a = 13.64 \text{ \AA}$ ,  $c = 11.27$ ,  $\beta = 128.0^\circ$ .

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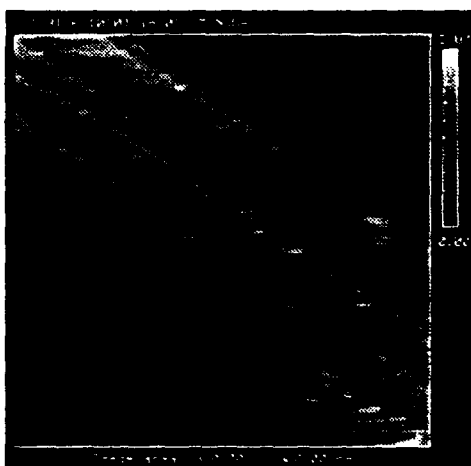


Figure 1a.

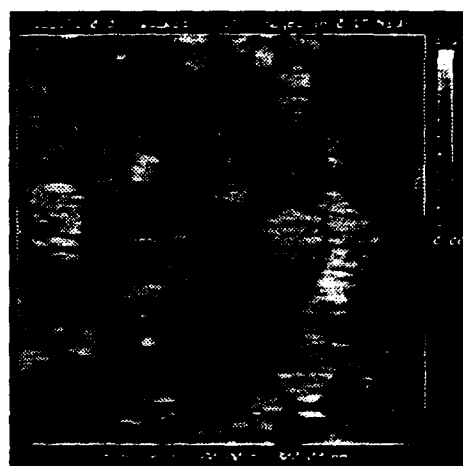


Figure 1b.

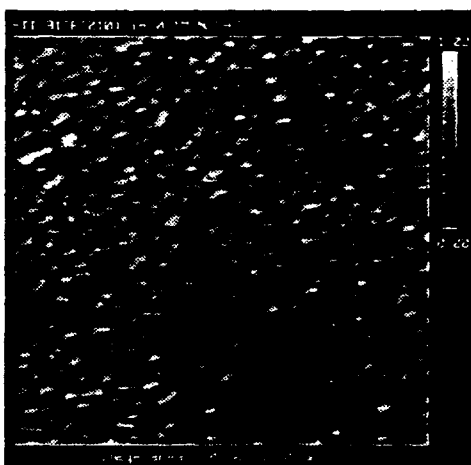


Figure 2a.

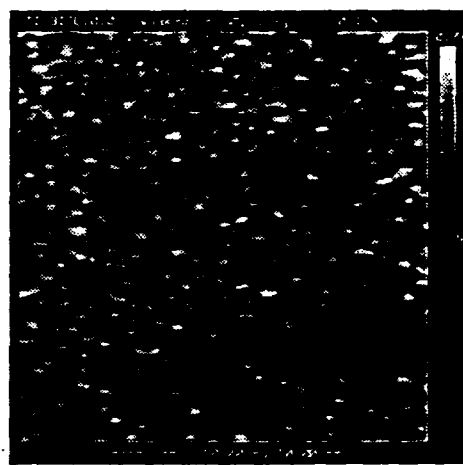


Figure 2b.

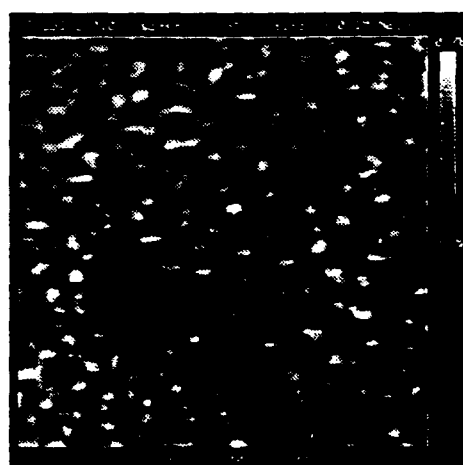


Figure 2c.

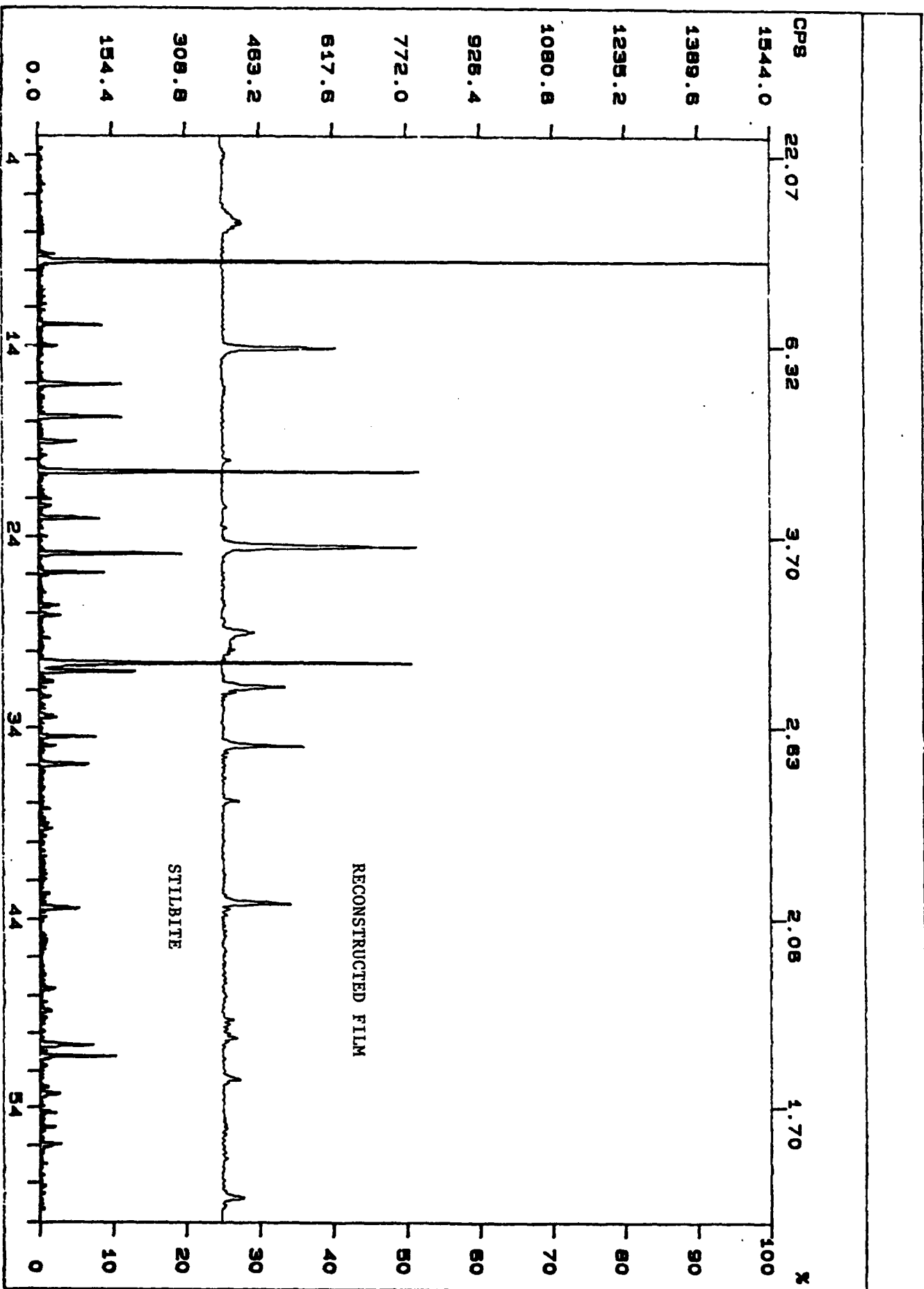
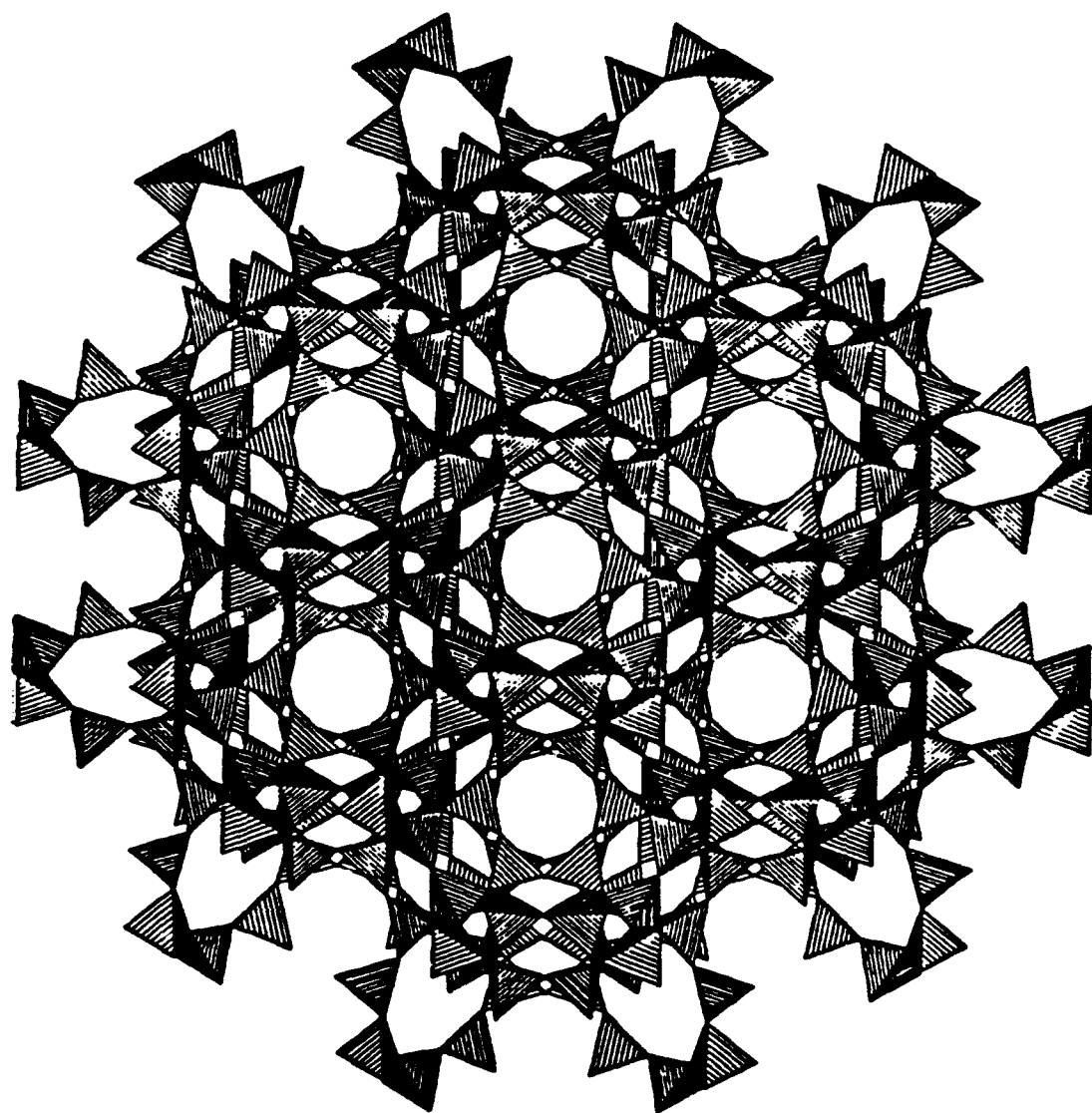


Figure 3.



Zeolite A [111] View  
Figure 4.

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